

1 That Which Is Claimed Is:

2 1. A process for forming a hybrid conversion coating on a ferrous metal substrate,  
3 comprising the steps of:

4 (a) applying to the substrate an intermediate coating rich in molecular iron and  
5 oxygen.

6 (b) contacting the coated substrate of step (a) with an aqueous solution of oxidizing  
7 agents to form a surface which is predominantly magnetite,  $\text{Fe}_3\text{O}_4$ .

8 2. The process of claim 1, wherein in step (a) the substrate is coated with a water insoluble  
9 dicarboxylate coating by contacting the substrate with an aqueous solution of a  
10 dicarboxylic acid at a concentration, pH, temperature and time to achieve a desired  
11 dicarboxylate coating.

12 3. The process of claim 1, wherein in step (a) the substrate is coated with a water insoluble  
13 iron phosphate coating by contacting the substrate with an aqueous solution of a reagent  
14 selected from phosphoric acid, pyrophosphoric acid and salts and mixtures thereof, at a  
15 concentration, pH, temperature and time to achieve a desired phosphate coating.

16 4. The process of claim 1, wherein in step (b) the coated substrate from step (a) is contacted  
17 with an aqueous solution of an oxidizing agent at a concentration, pH, temperature and  
18 time to form a coating of the desired amount of magnetite.

19 5. The process of claim 2, wherein in step (a), the dicarboxylic acid is selected from oxalic  
20 acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, maleic acid,  
21 malic acid, tartaric acid, citric acid and mixtures thereof.

22 6. The process of claim 5, wherein the dicarboxylic acid is oxalic acid at a concentration of  
23 about 3 - 35 grams per liter, a pH of about 0.5 - 2.5, a temperature of about 50 - 150° F,  
24 and a contact time of about 0.5 - 5.0 minutes.

25 7. The process of claim 4, wherein in step (b) the aqueous oxidizing solution contains  
26 oxidizing agents selected from alkali metal hydroxide at concentrations of about 25 - 200  
27 grams per liter, alkali metal nitrate at concentrations of about 9 - 70 grams per liter, and  
28 alkali metal nitrite at concentrations of about 1 - 10 grams per liter, a pH of about 13 - 14,  
29 a temperature of about 120 - 220° F, and a contact time of about 2 - 10 minutes.

30 8. The process of claim 1, further comprising the step of sealing the substrate with a topcoat  
31 after step (b).

32 9. The process of step claim 2, wherein in step (a) the substrate is coated in the presence of  
33 an additive selected from a grain refiner and an accelerator.

34 10. The process of claim 9, wherein the grain refiner is alkali metal tartrate at a concentration  
35 of about 0.1 - 1.0 gram per liter.

1       11. The process of claim 9, wherein the accelerator is selected from organic and inorganic  
2           nitro compounds, alkali metal salts of citrate, molybdate, polyphosphate, thiocyanate,  
3           chlorate and sulfide at concentrations of about 0.5 - 5.0 grams per liter.

4       12. The process of claim 3, wherein in step (a) the substrate is coated in the presence of an  
5           accelerator.

6       13. The process of claim 12, wherein the accelerator is selected from organic and inorganic  
7           nitro compounds at concentrations of about 0.1 - 5.0 grams per liter.

8       14. The process of claim 1, wherein the coated substrate from step (a) is contacted in step (b)  
9           with an aqueous solution of oxidizing agents in the presence of an additive selected from  
10          an accelerator, a metal chelator and a surface tension reducer.

11      15. The process of claim 14, wherein the accelerator is selected from alkali metal salts of  
12           molybdate, vanadate, tungstate, thiocyanate, dichromate, stannate, thiosulfate, stannous  
13           chloride, and stannic chloride at concentrations of about 0.05 - 0.5 grams per liter.

14      16. The process of claim 14, wherein the metal chelator is selected from alkali metal salts of  
15           thiosulfate, sulfide, ethylene diamine tetraacetate, thiocyanate, gluconate, citrate or  
16           tartrate at concentrations of about 1.0 - 10.0 grams per liter.

17      17. The process of claim 14, wherein the surface tension reducer is selected from  
18           alkylnaphthalene sulfonate at concentrations of about 0.025 - 0.2 grains per liter.

19      18. A ferrous metal article prepared according to any of claims 1 through 17.

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21      19. A coated colored ferrous metal article having a surface formed by two treatments,  
22           wherein the first treatment comprises an iron/oxygen-enriched intermediate oxidized  
23           coating formed on the ferrous metal article, and the second treatment comprises a further  
24           oxidation of the first coating to convert the first coating to a magnetite coating on the  
25           ferrous metal article.

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27      20. An oxidation solution for oxidizing at least a portion of an iron/oxygen enriched  
28           intermediate coating on a ferrous substrate to magnetite comprising an aqueous solution  
29           of oxidizing agents selected from alkali metal compounds of hydroxide, nitrate, and  
30           nitrite and mixtures thereof.

31      21. The oxidation solution of claim 20, and further including an additional component  
32           selected from an accelerator, a metal chelator, a surface tension reducer and mixtures  
33           thereof.

34      22. The oxidation solution of claim 20, wherein the oxidizing agents are sodium hydroxide,  
35           sodium nitrate and sodium nitrite.

1 vanadate, chlorate, tungstate, thiocyanate, dichromate, stannate, sulfide and thiosulfate,  
2 and stannous chloride and stannic chloride, and mixtures thereof.

3 24. The oxidation solution of claim 21, wherein the metal chelator is selected from alkali  
4 metal compounds of thiosulfate, sulfide, ethylene diamine tetraacetate, thiocyanate,  
5 gluconate, citrate, and tartrate and mixtures thereof.

6 25. The oxidation solution of claim 21, wherein the surface tension reducer is selected from  
7 alkyl naphthalene sulfonate and related compounds which are stable in high pH  
8 environments.

9 26. The oxidation solution of claim 25 at a pH range of about 12.0 - 14.0.

10 .27. A process for forming a hybrid conversion coating on a ferrous metal substrate,  
11 comprising the steps of:

12 (1) subjecting the ferrous metal substrate to treatment selected from cleaning,  
13 degreasing, descaling, and mixtures thereof;

14 (2) rinsing the substrate from step (1) with water;

15 (3) subjecting the substrate from step (2) to a first oxidation to form a molecular  
16 iron/oxygen enriched intermediate coating;

17 (4) rinsing the substrate from step (3) with water;

18 (5) subjecting the substrate from step (4) to a second oxidation to form a  
19 predominantly magnetite,  $Fe_3O_4$  coating;

20 (6) rinsing the substrate from step (5) with water; and

21 (7) sealing the substrate with an appropriate topcoat.

22 28. The process of claim 4, wherein in step (b) the aqueous oxidizing solution is at a  
23 temperature of about 70 - 120 F, and a contact time of about 10 to about 30 minutes.  
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